Characterising the within-field scale spatial variation of nitrogen in a grassland soil to inform the efficient design of in-situ nitrogen sensor networks for precision agriculture

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Characterising the within-field scale spatial variation of different N forms in a grassland soil and the implications for in-situ N sensor technology and precision agriculture

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ABSTRACT

The use of in-situ sensors capable of real-time monitoring of soil nitrogen (N) may facilitate improvements in agricultural N-use efficiency (NUE) through better fertiliser management. Optimising the deployment of in-situ sensors for both accuracy and cost requires consideration of the spatial variation of N forms at within-field scales. In this study, a geo-statistical nested sampling approach was used to characterise the spatial variability of amino acids, ammonium (NH_4^+) and nitrate (NO_3^-) in the soil of a grazed grassland field (1.9 ha). Within the growing season, two nested sampling campaigns were undertaken both before and after the application of fertiliser N and the removal of grazing sheep. The field was stratified into four quarters with four mainstations located at random within each quarter. Within each mainstation, sampling at the following spatial scales: 1 cm, 10 cm, 50 cm and 2 m, was performed using a soil corer with a 1 cm diameter. Further investigation into small-scale spatial variance was investigated using smaller soil samples (approx. 70 mg) that represented the "aggregate" scale. Short-range variation was found to be dominant, with at least 61%, 86% and 61% of the total accumulated variance of amino acid-N, NH_4-N and NO_3-N, respectively, occurring at scales < 2 m. Variation at larger scales (> 2 m) was not as significant but was still considered an important spatial component for all N forms. Fertiliser N application and removal of sheep had a small effect on the spatial variance of N forms. In the case of NO_3-N, the total accumulated variance was lower, with more of the observed variance attributed to scales > 2 m. The aggregate-scale sampling revealed further large variation at the sub 1-cm scale. Calculations based on the sampling showed that the NO_3-N field mean could be estimated with a 95% confidence interval of 1.69 µg N g^{-1} using 2 randomly positioned data loggers each with 5 sensors. These calculations assume that the sensor used would sense a similar volume of soil to that sampled by the 1 cm soil corer. Sensors with sensing elements < 1 cm will be subject to further spatial variability and local

replication at scales < 1 cm would be needed to maintain accuracy. Therefore, achieving accurate estimates of the field mean is likely to incur significant costs. Whilst the cost of technology is likely to decrease, investigation of how best to integrate this approach within a precision agriculture framework to improve NUE is still required.

Keywords: Dissolved organic nitrogen; Fertilizer management; Nutrient cycling; Soil heterogeneity

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1. Introduction

Improving nitrogen (N) use efficiency (NUE) remains one of the key challenges for global agriculture (Cassman et al., 2002; Robertson and Vitousek, 2009) and is essential for the success of sustainable intensification (Tilman et al., 2011). The deleterious environmental effects and economic costs of diffuse N pollution from farmland in Europe, where N has been applied in excess of crop requirement, are well documented (Sutton et al., 2011).

One often cited approach to reduce N losses and improve NUE, is to ensure synchronicity of N supply with crop demand (Shanahan et al., 2008; Robertson and Vitousek, 2009), although, achieving this in practice is challenging due to the complex nature of the soil-plant system. Precision agriculture (PA) attempts to address this issue by reducing uncertainties surrounding the measurement of key variables to determine optimum N fertiliser management (Pierce and Nowak, 1999; Dobermann et al., 2004). Key to the success of PA is the accurate assessment of within-field soil N status at a high spatial and temporal resolution to enable the variable rate application of N fertiliser. This approach allows areas of N deficiency and surplus to be addressed as well as in-season adjustment of fertiliser rates in accordance with current and predicted growing conditions. However, conventional soil sampling techniques, coupled with laboratory analysis are expensive, labour-intensive, and time-consuming and cannot provide real-time data of sufficient resolution to accurately inform PA management (Sylvester-Bradley et al., 1999; Kim et al., 2009).

A number of different approaches have been used to address this issue. Crop canopy sensing techniques, for determination of plant N status, are now in commercial use and can be used to inform variable rate fertiliser application (e.g. wheat, maize; Raun and Johnson, 1999; Diacono et al., 2013). Whilst the advantages of this approach in some situations have been evidenced (Diacono et al., 2013), plant N status and yield is the product of many variables and may not always correlate with soil mineral N status. On-the-go soil sampling

for nitrate, using electrochemical sensor platforms attached to agricultural vehicles have been developed (Adsett et al., 1999) and, for the case of pH, commercialised (Adamchuk et al., 1999). The results have been used to develop field nitrate maps (Sibley et al., 2009) which could be used to define within-field management zones and to calculate variable fertiliser application rates. On-the-go sampling is generally more spatially intensive than manual field sampling, allowing better spatial resolution, although key information on how soil mineral N varies over small spatial scales may not be obtained. This can lead to increased uncertainties of interpolative predictions, especially if the sample volume is small (Schirrmann and Domsch, 2011). Furthermore, increasing the temporal resolution of this approach requires additional economic costs and as both these approaches rely on reactive management, crucial changes in soil mineral N status may be missed.

One approach, which has yet to be explored, is the use of in-situ sensors capable of monitoring soil mineral N in real time. This approach may enable a step away from predetermined fertiliser N recommendations (Defra, 2010) to a more dynamic system that responds in real-time to changes in growing conditions. It potentially has many benefits compared to on-the-go soil sampling and crop canopy sensing. The data provided by in-situ sensors will be of significantly higher temporal resolution, negating the need for repeated sampling surveys throughout the year, which represent an economic cost to the farmer. Furthermore, this may enable more accurate timing of fertiliser application, reducing the risk of yield penalties caused by N-nutrition deficiencies, and reducing the risk of N transfers to water and air as a result of excessive fertiliser N applications. It is also likely that the high resolution data generated by an in-situ sensor network will increase knowledge of the controls of soil N processes and thus enable development of models which allow for a proactive approach to fertiliser N management.

93 At the time of writing, there are no such quasi-permanent field sensors in use
94 commercially. However, potential for the development and deployment of such sensors exists
95 (Shaw et al., 2014). Ion-selective electrodes have many characteristics suitable for soil
96 sensing networks. They are relatively cheap, simple to use, require no mains electrical power
97 supply and the concentration of the target ion can be easily calculated via a pre-calibration.
98 Nitrate (NO_3^-) selective electrodes have previously been successfully deployed for
99 monitoring streams and agricultural drainage ditches (Le Goff et al., 2002; Le Goff et al.,
100 2003) as well as for on-the-go soil sampling of agricultural soils (Sinfield et al., 2010) and
101 on-farm rapid tests for soil NO_3^- (Shaw et al., 2013). Direct soil measurement, which is
102 essential for the success of in-situ monitoring, has been shown to be possible (Ito et al., 1996;
103 Adamchuk et al., 2005), although improvements in accuracy and robustness of the sensing
104 membrane are required. Increasing use of nano technologies for the construction of
105 electrochemical sensors may result in significant advances in sensor performance (Arrigan,
106 2004; Atmeh and Alcock-Earley, 2011).
107 Optimising the spatial configuration of a sensor network is needed to ensure that
108 precise estimate of the mean across a field or management zone can made whilst minimising
109 economic costs. It is, therefore, important to make an assessment of the spatial variation of
110 soil mineral N across a range of scales to determine an optimum configuration prior to
111 implementation of the sensor network. This is particularly important in grazed grasslands
112 where N returns from livestock occur unevenly (Bogaert et al., 2000). Since sensors must be
113 organized in clusters around a hub with a logger, sensor networks can be regarded as multi-
114 scale sampling schemes with hubs, the primary units, and sensors (secondary units) randomly
115 placed in an area around each hub. As shown by de Gruijter et al. (2006), the optimum
116 configuration of such a sampling scheme depends on the relative costs of additional primary
117 and secondary units and the within- and between-primary unit variability. For example a field

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which has little large-scale variation may be served by a collection of sensors connected to one sensing hub, whereas a field with more variation at larger scales would require sensors to be located in multiple areas of the field. When determining an optimal configuration it is also important to consider the degree of uncertainty of the resulting estimations and the associated cost-benefit of reducing this uncertainty. Consideration also needs to be made as to whether the scale and magnitude of the observed in-field N variation is large enough to justify spatial variation in the optimum fertiliser input rate and, hence, the demarcation of within-field management zones.

As seen in the discussion above, the feasibility and optimal design of sensor networks depends on the variability of the target properties at different within-field scales. An effective way to collect such information is by spatially nested sampling. This was first used in soil science by Youden and Mehlich (1937) and rediscovered as a technique for investigation of multiscale soil variation by Webster and Butler (1976). In nested spatial sampling, sample sites are arranged in a nested hierarchical design which allows the partition of the variance of the measured variable into components associated with a set of pre-determined scales. At the highest level of the hierarchy sample, points are arranged in clusters associated with "main stations" which may be at randomly-located sites or on nodes of a grid or transect. Within a mainstation, sample points may be divided between two or three stations at level 2 which are separated from each other by some fixed distance. For example, the stations at level 2 may be on the vertices of an equilateral triangle with sides length d_2 m, or at two locations d_2 m apart. While these distances are fixed, the orientation of the level-2 stations relative to each other is randomized to ensure lack of bias. Within each level-2 station, sample points may be ordered at further nested spatial scales.

This approach has been used to investigate the distribution of nematodes in soil at within-field scales (Webster and Boag, 1992), to examine the variation of ammonia

143 volatilization from urea amended soil at within-field to landscape scales (Corstanje et al.,
144 2008), to resolve the spatial variability of soil N mineralisation (Córdova et al., 2012), and to
145 examine the interactions of soil and herbicide at within-field scale (Price et al., 2009).
146 Recently, Lark (2011) showed how setting nested sampling in the linear mixed model
147 framework allows the nested sampling scheme to be optimized in different circumstances.

148 The aim of this study was to investigate the spatial variation of plant-available N
149 (amino acids, ammonium (NH_4^+) and NO_3^-) concentrations in soil within a grassland field
150 over a 2 month period. A geo-spatial statistical approach was used to quantify the observed
151 variation and the results were used to explore how an in-situ soil N sensor network may be
152 optimally designed and deployed. The potential and challenges of integrating this approach
153 within a PA framework are discussed.

154

155 **2. Materials and methods**

156 *2.1. Field site and soil characteristics*

157 The field used for this study is located within the Henfaes Research Station
158 Abergwyngregyn, Wales, UK (53°14′N 4°01′W). The site has a temperate, oceanic climate,
159 receives an average annual rainfall of 1250 mm and has a mean annual soil temperature at
160 10 cm depth of 11 °C. The field is roughly rectangular with a perimeter of 559 m and an area
161 of 1.91 ha. It has an average altitude of 12.1 m asl with a slope of 1.5 % in a northerly aspect.
162 It is a semi-permanent sheep-grazed grassland, dominated by *L. perenne* L. The current ley
163 was established by direct drill in April 2009 using a perennial and hybrid ryegrass mix. The
164 field has been used for both all year round grazing and silage production since 2009,
165 receiving an annual inorganic fertiliser input of between 100 – 130 kg N ha^{-1} in addition to
166 potassium (K), phosphate (P) and sulphur (S) at recommended rates. Lime has also been
167 applied when necessary to restore the pH to a target value of 6.5. In 2014, inorganic fertiliser

was applied on 12/5/14 and 11/7/14 at a rate of N:P:K 50:10:10 and 60:4:0 kg ha^{-1}, respectively. The field was grazed until 9/6/14 and the field remained sheep free until the 2/9/14. The soil is a free draining Eutric Cambisol with a sandy clay loam texture and a fine crumb structure.

To assess the chemical characteristics of the soil, replicate samples (n = 4) were collected from 4 blocks (30 × 30 cm) at a depth of 0 – 10 cm, representing the Ahp horizon. The soil was placed in gas-permeable polyethylene bags and transported to the laboratory in a refrigerated box. All of the following procedures were performed on the same day as field sampling. Soil pH and electrical conductivity were determined in a 1:2.5 (w/v) soil:distilled water suspension using standard electrodes. Moisture content was determined by drying for 24 h at 105 °C. Total C and N were determined with a TruSpec CN analyser (Leco Corp., St Joseph, MI, USA). Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) were measured in soil extracts (0.5 M K_2SO_4, 1:5 w:v) using an Analytik Jena Multi N/C 2100S (AnalytikJena, Jena, Germany). Chloroform fumigation and incubation (t = 7 days) of 2 g (n = 4) of fresh soil was performed to determine microbial biomass C and N according to Voroney et al. (2008) (K_{EC} = 0.35 K_{EN} = 0.5). Exchangeable cations were extracted using 0.5 M acetic acid (Sparks, 1996) and the filtered extracts analyzed using flame emission spectroscopy (Sherwood 410 flame photometer; Sherwood Scientific, Cambridge, UK). Extractable phosphorus (P) was determined by extraction with 0.5 M acetic acid with subsequent colorimetric analysis using the molybdate blue method of Murphy and Riley (1962). Basal soil respiration was determined in the laboratory at 20 °C using an SR1 automated multichannel soil respirometer (PP Systems Ltd., Hitchin, UK) and steady state CO_2 production rates recorded after 24 h. Potentially mineralisable N was determined using an anaerobic incubation method based on Keeney (1982). Briefly, 5 g field moist soil was place in a 50 ml centrifuge tube, which was then filled to the top with de-ionized H_2O and the

tubes sealed. Soils were subsequently incubated in the dark at 40 °C for 7 d. The difference in NH_4^+ content between t = 0 and t = 7 d was attributed to N mineralization. Above ground biomass was sampled on 26/6/2014. Replicate 1 × 1 m blocks (n = 4) were chosen at random from within the field. The vegetation was cut to ground level, stored in paper bags and subsequently oven-dried at 80 °C to determine dry matter content. A summary of the results are shown below in Table 1.

2.2. Sampling design and protocol

Nested sampling for spatial variability: The sampling was designed in the light of the following considerations. The aim was to characterize the variability of forms of soil N at a range of spatial scales relevant to planning the design of an in-situ sensor network. In particular, it was necessary to examine the relative importance of variance between and within local regions each of which might be represented by a cluster of NO_3^- electrodes or similar sensors deployed around a single data logger such that the maximum distance between any two sensors is about 2 m. In a grassland environment it was expected that one source of variation would be urine patches of linear dimensions about 40 cm (Selbie et al., 2015). Otherwise we had no prior information on the likely distribution of variance between the scales of interest.

Given these considerations we planned a nested sampling design with length scales within each main station of 1 cm, 10 cm (intermediate between the fine scale and urine patch scale), 50 cm (urine patch scale) and 2 m (upper bound on the "within-region served by a sensor cluster" scale). We distributed mainstations by stratified random sampling with the target field divided into four quarters (strata) of equal area. Four mainstations were established at independently and randomly-selected locations within each quarter (stratum), giving a total of 16 mainstations. The design of the sampling scheme within each mainstation

218 was obtained by the optimization procedure of Lark (2011) on the assumption of a fractal or
219 quasi-fractal process in which the variance is proportional to the log of the spatial scale. The
220 objective function was the mean estimation variance of the variance components. Figure 1
221 shows the optimized sample design. With 12 samples per mainstation the total sample size
222 was 192. The sample sites were then selected at each mainstation by randomizing the
223 direction of the vectors between the substations at each level of the design shown in Figure 1,
224 while keeping the lengths of the vectors fixed. An initial nested sampling campaign was
225 performed over 2 days on the 4th and 5th June, 2014. This was repeated on the 31st July and 1st
226 August, 2014, 3 weeks after the field received a N fertiliser input of 60 kg N ha^{-1}. Sample site
227 locations were set up the day before sampling took place. At each sampling location a soil
228 corer, of diameter 1 cm, was used to sample soil. A 5 cm soil core from between depths of 5 -
229 10 cm was sampled and placed in gas-permeable plastic bags, and stored in a refrigerated
230 box. This depth was chosen as it represents the middle of the rooting zone and would make
231 installation of any in-situ sensor a straight forward process. Following the sampling event the
232 samples were transferred immediately to the laboratory where they were refrigerated at 4 °C.
233 Extraction of soluble N from soil was performed on the soil cores on the same day as
234 sampling as described below. During the second nested sampling event, duplicate sub-
235 sampling and chemical analysis were performed on 4 out of the 12 samples from each
236 mainstation in order to make an assessment of measurement error.

237 To investigate spatial variability of N forms at the sub-core scale a further sampling
238 design and protocol was developed and performed on the 25th June, 2014. Two sampling
239 locations were chosen at random within each of the 4 strata. At each location, a pair of
240 samples were taken, using the protocol described above, with a distance of 1 cm between
241 each sample. This resulted in a total of 16 core samples. On return to the laboratory the cores
242 where broken apart and 4 “aggregates” of weight 60 – 80 mg were collected (diameters ca. 1-

2 mm). These aggregates were then soluble N extracted and analysed using the protocol described below.

Investigating depth effects: To investigate the variability of forms of N with depth an equilateral triangle, with sides 50 cm, was randomly located within each strata. The 50 cm scale was chosen as the initial nested sampling showed that it encompassed most of the variance for all N forms. At the vertices of the triangle, a core was taken to 25 cm depth and was subsequently split into 5 cm sections, giving a total of 60 samples. This sampling was performed on the 27th June, 2014.

2.3. Extraction and chemical analysis of soil samples

All soil extractions were performed on the same day as sample collection, according to the following protocol. Samples were crumbled by hand, in order to prevent sieving induced N mineralisation (Jones and Willett, 2006; Inselsbacher, 2014). Large stones, roots and vegetation were removed prior to gentle mixing of the sample. To further reduce mineralisation of organic N forms, sub-samples of field-moist soil (2 g) were extracted on ice (175 rev min^{-1}, 15 min) using cooled (5 °C) 0.5 M K_2SO_4 at a soil: extractant ratio of 1:5 (w:v) (Rousk and Jones, 2010). The extracts were centrifuged (4,000 *g*, 15 min), and the resulting supernatant collected and frozen (-18°C) to await chemical analysis. The protocol differed slightly for the soil aggregate samples. Each aggregate, of weight 60 – 80 mg, was placed in a 1.5 ml Eppendorf® micro-centrifuge tube and crumbled gently using a metal spatula. The soil was then extracted in 500 µl of 0.5 M K_2SO_4 as described above. Total free amino acid-N was determined by the *o*-phthaldialdehyde spectrofluorometric method of Jones et al. (2002). NH_4-N was determined by the salicylate-nitroprusside colorimetric method of Mulvaney (1996) and NO_3-N by the colorimetric Griess reaction of Miranda et al. (2001) using vanadate as the catalyst.

268

269 *2.4. Statistical analysis*

270 *Nested Sampling:* The *n* data from the nested sampling may be analysed according to
271 the following statistical model. An $n \times 1$ vector of observations, **y**, is regarded as a
272 realization of a random variate, Y, where

273 $$Y = X\beta + U_s\eta_s + U_m\eta_m + U_2\eta_2 + U_{0.5}\eta_{0.5} + U_{0.1}\eta_{0.1} + U_{0.01}\eta_{0.01} + U_r\eta_r. \quad (1)$$

274 X is a $n \times p$ design matrix which represents fixed effects in the model (e.g. p levels
275 of a categorical factor, or p continuous covariates) and β is a length-p vector of
276 fixed effects coefficients. There are 4 strata in the sampling design, and U_S is a $n \times$
277 4 design matrix for the strata. If the ith observation is in stratum j then $U_S[i, j] =$
278 1 and all other elements in the ith row are zero. The design matrix associates each
279 observation with one of 4 random values in the random variate η_s. These values
280 are assumed to be independent and identically distributed Gaussian random variables with
281 a mean of zero and a variance σ^2_s which is the between-stratum variance component.
282 Similarly U_m is a $n \times 16$ design matrix for the mainstations, and the variance of
283 η_m is the between-mainstation variance component. The terms with subscripts 2, 0.5. 0.1 and
284 0.01 represent the design matrices and random effects for the components of variation
285 associated with the 2-m, 0.5-m, 0.1-m and 0.01-m scales respectively. If duplicate material
286 from some or all of the soil specimens is analysed then the random effect η_r which represents
287 the variation due to subsampling and analytical variation can be estimated, otherwise it is a
288 component of the variation estimated for the finest spatial scale.

289 Under the linear mixed model Y has covariance matrix H where

290 $$\mathbf{H} = \sigma^2_s U_s^T U_s + \sigma^2_m U_m^T U_m + \sigma^2_2 U_2^T U_2 + \sigma^2_{0.5} U_{0.5}^T U_{0.5} + \sigma^2_{0.1} U_{0.1}^T U_{0.1}$$

291 $$+ \sigma^2_{0.01} U_{0.01}^T U_{0.01} + \sigma^2_r U_r^T U_r, \quad (2)$$

292 and the superscript T denotes the transpose of a matrix. The parameters of this matrix are
293 therefore the variance components, and these can be estimated by residual maximum
294 likelihood (REML), see Webster and Lark (2013). Once this has been done then the fixed
295 effects coefficients in the model can be estimated by generalized least squares (see Lark and
296 Cullis, 2004). Note that there is an explicit assumption that the data are a realization of a
297 Gaussian random variable. For this reason the values were transformed if exploratory
298 analysis suggested that this is not a plausible assumption.

299 Because all sampling could not be done in one day the sampling day was randomized
300 within strata, so as not to be confounded with the spatial variance components of interest. For
301 this reason it is regarded as a fixed effect in the model. The significance of the between-day
302 effect was tested with the Wald statistic as discussed in Lark and Cullis (2004).

303 The significance of a random effect in the model can be tested by comparing the
304 residual log-likelihood for a model with the term dropped (L^-) with the residual log-
305 likelihood for the full model (all random effects, L). Any variance accounted for by a term
306 which is dropped will contribute to variance at lower levels in the hierarchy (finer spatial
307 scales) for the dropped model. For this reason the ultimate component of the model (η_r when
308 there are duplicate analyses and $\eta_{0.01}$ otherwise) cannot be dropped. Dropping a term from
309 the model will usually reduce the log-likelihood (and will not increase it). Whether the
310 reduction in likelihood is strong enough evidence that the inclusion of the term in the full
311 model is justified can be assessed by computing Akaike's information criterion *AIC* for each
312 model:

313 $$AIC = -2L + 2P \qquad (3)$$

314 where P is the number of parameters in the model. The *AIC* penalizes model complexity, by
315 selecting the model with smaller AIC, one minimises the expected information loss through
316 the selection decision (Verbeke and Molenberghs, 2000).

317 *Aggregate scale sampling:* After any necessary transformations the *n* data collected to
318 investigate variation within cores were analysed according to the following statistical model.
319 An $n \times 1$ vector of observations, y, is regarded as a realization of a random variate, Y, where

320 $$Y = X\beta + U_s\eta_s + U_p\eta_p + U_c\eta_c + U_a\eta_a, \quad (4)$$

321 As in Equation (1), X is a design matrix for fixed effects and β is a vector of fixed effects
322 coefficients (here just a constant mean). Again, as in Equation (1), U_s is a $n \times 4$ design
323 matrix for the strata and η_s is assumed to be an independent and identically distributed
324 Gaussian random variate with a mean of zero and a variance σ^2_s. In the same way U_p and η_p
325 are the design matrix and the random variate for the between-pair within stratum effect, with
326 variance σ^2_p; U_c and η_c are the design matrix and the random variate for the between-core
327 within-pair component, with variance σ^2_c and U_a and η_a are the design matrix and the random
328 variate for the between-aggregate within-core component, with variance σ^2_a. This latter
329 component is effectively the residual as there are no duplicate measurements on any
330 aggregate. The same method based on the AIC was used to assess the evidence for including
331 each term in the model above the between-aggregate effect.

332 *Depth sampling:* After any necessary transformation the data were analysed by a
333 nested linear mixed model of the form

334 $$Y = X\beta + U_s\eta_s + U_c\eta_c + \varepsilon. \quad (5)$$

335 As in previous models X is a design matrix for fixed effects, here associating each
336 observation with one of the five depth increments. The fixed effects coefficients in β are
337 therefore mean values of the target variable for each increment. As before U_s and U_c are
338 design matrices for between-stratum and between-core-within-stratum random effects. The
339 term ε is an identically and independently distributed random variable of mean zero, the
340 residual. This model was fitted by REML, and Wald tests were used to test the null
341 hypothesis of equal mean values for the depth increments.

342

343 *2.5. Design of sensor arrays*

344 The variance components derived from the nested sampling were used to examine the
345 theoretical performance of different configurations of an in-situ sensor array, where a cluster
346 of n_e sensors are randomly located within a region of 2 m diameter around each of n_l data
347 logging hubs, which are located by simple random sampling. The between-sensor within-
348 logger component of variance can be approximated by

349 $$\sigma^2_{sens} = \sigma^2_2 + \sigma^2_{0.5} + \sigma^2_{0.1} + \sigma^2_{0.01}, \quad (6)$$

350 and the between-logger variance by

351 $$\sigma^2_{log} = \sigma^2_s + \sigma^2_m. \quad (7)$$

352 As such, the standard error of the mean can be estimated as follows:

353 $$\sigma_{mean} = \{(\sigma^2_{log} / n_l) + (\sigma^2_{sens} / n_l n_e)\}^{½} . \quad (8)$$

354 The 95% confidence interval of the mean could therefore be calculated given variance
355 components and particular values of n_l and n_e and the limits were back-transformed to the
356 original units of measurement.

357

358 **3. Results**

359 *3.1. Nested sampling to evaluate the spatial distribution of soluble N in soil prior to*
360 *application of N fertiliser*

361 Table 2 shows summary statistics for amino acid, NH_4^+ and NO_3^- concentrations in
362 soil for the nested sampling undertaken over 2 days in June. Note that in all cases a Box-Cox
363 transformation was chosen, conditional on sampling day as a fixed effect. Variance
364 components for the different spatial scales are shown in Table 3 and the accumulated
365 variance components, from the smallest to largest scale, are plotted in Figure 2. In total, 192
366 samples were collected and processed over 2 days.

The results show that there was a significant difference (as assessed by the Wald statistic) between the 2 sampling days for NH_4-N concentration only. The different forms of N showed slightly different scale-dependencies, although in general, short-range variance dominated. For amino acid-N, the 1-cm scale had the largest variance component, constituting 58.6% of the total accumulated variance. The 10-cm and the between-mainstations within strata term were important spatial components as they were judged by the AIC to improve the likelihood of the model sufficiently to justify their inclusion. Similarly, for NH_4-N the 1-cm scale had the largest variance component, constituting 63.0% of the total accumulated variance. However, for spatial scales greater than 1 cm, only the between-mainstations within strata term was important as judged by the AIC. For NO_3-N, there was more variance at larger scales compared to the other forms of N, with the 10-cm scale having the largest variance component, constituting 28.0% of the total accumulated variance. Furthermore, all the spatial scales, with the exception of the 2-m scale, exhibit variance that was considered important by the AIC. Short-range scale variation still dominated though, with 70.4% of the variance occurring at spatial scales up to 50 cm. It should be noted that the 1-cm scale component will also include any measurement error.

3.2. Nested sampling to evaluate the spatial distribution of soluble N in soil after application of N fertiliser

To assess the influence of nutrient management regime, a second nested sampling was undertaken in July, 3 weeks after the field had been fertilised with 60 kg N ha^{-1}. Summary statistics for soluble N in soil are shown in Table 4 and variance components for the different spatial scales are shown in Table 5.

The accumulated variance components, from the smallest to largest scale, are plotted in Figure 3. The same protocol was used as for the first nested sampling with the addition of

duplicate measurements on 4 samples from each mainstation. This allowed the 1-cm spatial variance component to be resolved from the subsampling and measurement error, which is the residual variance in this analysis. As this forms the ultimate term in the model, it allows an assessment of the importance of the 1-cm spatial component by the AIC. For all of the N forms, the 1-cm scale was considered important by the AIC, and was larger than the residual variance. However, the residual variance, which was similar for all N forms, constitutes a substantial component of the accumulated variance and was, for all N forms, larger than the variance at 50 cm and 2 m. The different forms of N showed slightly different scale-dependencies, although in general short-range variance dominated. For amino acid-N the between mainstations within strata had the largest variance component, constituting 35.8% of the total accumulated variance, although 57.7% of the total accumulated variance occurred at scales up to 10 cm. The 1-cm, 10-cm and the between-mainstations within-strata term were important as they are judged by the AIC to improve the likelihood of the model sufficiently to justify their inclusion. For NH_4-N, the 1-cm scale had the largest variance component, constituting 55.1% of the total accumulated variance. Spatial scales greater than 10 cm accounted for only 13.3% of the total accumulated variance. Only the 1-cm and the between-mainstations within-strata terms were important as judged by the AIC. For NO_3-N, the variance at larger scales was similar to that of amino acids, with the the between-mainstations within strata scale having the largest variance component, constituting 38.7% of the total accumulated variance. As for amino acid-N, the 1-cm, 10-cm and the between-mainstations within-strata term were important as they are judged by the AIC. Short-range scale variation still dominated though, with 61.2% of the variance occurring at spatial scales up to 50 cm.

3.3. Aggregate-scale variability of soluble N in soil

The grassland soil is characterized by small aggregates (ca. 1-2 mm diameter) relative

417 to the size of the bulk soil cores used in the nested samplings (1 cm diameter). Table 6 shows
418 the summary statistics for the within-core, aggregate scale variability while the variance
419 components are shown in Table 7.

420 In all cases, the largest variance component was the between-aggregate within-core
421 scale. For NH_4-N and NO_3-N, 91.3% and 80.1% respectively of the total accumulated
422 variance occurred at this scale, which was an order of magnitude higher than the variance at
423 the between core scale. The variance at the aggregate scale for amino acid-N was slightly
424 lower at 69.2%. It should be noted that any analytical error that occurred will also appear in
425 this variance component. The between-core component, which represents the 1-cm spatial
426 scale, was important for amino acid-N and NO_3-N, but not NH_4-N, as judged by the AIC.
427 Neither the between-pair component, which is similar to the between-mainstations scale, nor
428 the between-strata component were found to be important as judged by the AIC. Due to the
429 limited replication (2 pairs of cores per strata), the results at stratum and mainstation scale
430 should be interpreted in light of the above nested sampling results. The main interest is in the
431 relative magnitude of the between-core within-pair and between-aggregate within-core
432 components of variance.

433

434 *3.4. Influence of depth of the variability of soluble N in soil*

435 Table 8 shows summary statistics for residuals of the Box-Cox transformed data
436 collected from different soil depths. All forms of N showed a decreasing trend down the soil
437 profile (Figure 4). Table 9 presents the estimated mean values for all N forms (Box-Cox
438 transformed) for each depth increment. There is a clear reduction in the concentration of each
439 N form with depth. The variation with depth was significant for NH_4-N and NO_3-N ($p <$
440 0.001) but not for amino acid-N ($p = 0.55$).

441

442 *3.5. Optimisation of a within-field sensor network for monitoring soluble N in soil*

443 Figure 5 shows plots of the width of the 95% confidence interval for NO_3-N using
444 variance components from the two sets of spatially nested samples. These were computed for
445 n_l =1–10 loggers with n_e =2–15 sensors distributed equally among the loggers, 15 being the
446 maximum number of sensor ports on the data logger (DL2e DeltaT, Cambridge, UK). The
447 total cost for each configuration is shown on the abscissa of the plot, on the basis of unit costs
448 of £2000 and £200 respectively for a data logger (DL2e DeltaT, Cambridge, UK) and an
449 ELIT NO_3^- electrode with a coupled reference electrode (ELIT 8021, ELIT 003, Nico2000,
450 Harrow, UK). The form of these curves reflects the distribution of the variance of NO_3-N
451 over the spatial scales. Note that the width of the confidence interval is largest for the June
452 observations, so discussion is focussed on these. Note also, as described in the Figure caption,
453 that some points are excluded from the plot (small numbers of sensors on small numbers of
454 loggers) to allow both graphs to be displayed with the same range of values on the ordinate.

455 The graphs show how both increasing the number of sensors per logger, and
456 increasing the number of loggers, reduces the width of the confidence interval. Note that
457 reducing this width substantially below 1 μg N g^{-1} dry soil would require substantial costs,
458 with small marginal improvement on increasing the size of the array. To reduce the width of
459 the confidence interval to 0.5 μg N g^{-1} dry soil requires 10 loggers with 11 sensors each at a
460 cost of £22,200.

461 The graphs allow different options for the design of arrays to be explored. If, for
462 example, we required the width of the 95% confidence interval to be no wider than 1 μg N g^{-1}
463 dry soil then the options include the use of 3 loggers with 11 sensors per logger, 4 loggers
464 with 5 sensors per logger or 5 loggers with 4 sensors per logger. The costs of these options
465 are £8,200, £9,000 and £10,800 respectively. This quality measure cannot be achieved with
466 just one or two loggers. The rational choice of array configuration is therefore 3 loggers with

467 11 sensors on each. Consider an alternative situation where the budget was fixed at £5,000.
468 This could be used to provide a single logger with 15 sensors on each, or two loggers with 5
469 sensors on each. The width of the confidence interval for these two options is ± 2.12 and ±
470 1.69 µg N g^{-1} dry soil respectively, so the second option is the rational choice.

471 The discussion above highlights that, with increasing budget, it is not necessarily
472 rational to use the maximum number of sensors on a logger before changing to an array with
473 an extra logger. However, once three or more loggers are in use, $n_l \geq 3$, an array of $15n_l$
474 sensors is always more efficient than any array of equal or lesser total cost with more than n_l
475 loggers.

476

477 **4. Discussion**

478 *4.1. Spatial variation of soluble N at within-field scales*

479 An assessment of the spatial variation of amino acid-N, NH_4-N and NO_3-N at within-
480 field scales was determined using a nested sampling approach. Short-range variation was
481 found to be dominant, with at least 61%, 86% and 61% of the total accumulated variance
482 amino acid-N, NH_4-N and NO_3-N, respectively, attributed to scales < 2 m. The aggregate-
483 scale sampling revealed further large variation at the sub 1-cm scale, which was considerably
484 higher than the variation attributed to the 1-cm scale for all N forms. Although short-range
485 variation dominated, variation at larger scales was not negligible and the within-strata,
486 between-mainstation scale was considered an important spatial component for all N forms.

487 It is likely that the observed variation at scales < 2 m is primarily due to the relatively
488 random and uneven deposition of N from sheep excreta. Similar small-scale variation of
489 NO_3-N in grazed pastures has been identified in previous studies, with semi-variograms
490 exhibiting the range of spatial dependency < 5 m (White et al., 1987; Broeke et al., 1996;
491 Wade et al., 1996; Bogaert et al., 2000), and a nugget variance of 60 % (Bogaert et al., 2000).

These results contrast with similar studies performed on arable soils, which were characterised by ranges of spatial dependencies for NO_3-N > 39 m (Van Meirvenne et al., 2003; Haberle et al., 2004).

Given that the linear dimension of a urine patch is approximately 40 cm, it is unlikely that the observed variation at the 1-cm and "aggregate" scales is driven by the uneven deposition of sheep excreta. Previous studies of spatial variation in soil N, in the context of within-field scales, have not investigated variation over such small scales. Variation at these scales is unlikely to have any significance for agronomic management as most soil sampling is conducted using large soil cores (ca. 2-10 cm diameter) with subsequent bulking of samples to ensure that small scale variation is encompassed. This small-scale variation is likely due to the inherent micro-heterogeneity of soil properties, for example, the abundance of plant roots and mycorrhizal hyphae (Stoyan et al., 2000), availability of labile organic matter (Parkin, 1987; Wachinger et al., 2000), earthworm channels and the composition and abundance of the microbial community (Grundmann and Debouzie, 2000; Nunan et al., 2002), which in turn will affect biogeochemical processes controlling soil N concentrations. The proportion of the total accumulated variance attributed to the 1-cm scale was much larger for amino acid-N and NH_4^+-N than NO_3-N which may be related to their relative diffusion coefficients, interactions with the solid phase (Owen and Jones, 2001) and the rapid rate of amino acid turnover and mineralisation in this soil (Jones et al., 2004; Wilkinson et al., 2014). The observed variation at larger spatial-scales within this study, could be due to the habit of sheep to frequent certain areas of the pasture such as paths, a drinking trough and areas of shade (Bogaert et al., 2000).

Variation with soil depth was also apparent, with all N forms showing a consistent reduction in concentration with increasing depth, although this was not considered a significant effect for amino acids. Decreasing concentrations of inorganic N down the soil

profile is well characterised in the literature (Van Meirvenne et al., 2003; Wall et al., 2010) and can be attributed to inputs of N via leaf litter, rainfall, animal excreta and fertilisers to the soil surface as well as being the site where maximal root turnover exists.

There was also some suggestion of a spatio-temporal interaction as evidenced by small differences in the spatial dependencies of the N forms between the June and July nested sampling events. In the case of NO_3-N, the total accumulated variance was lower, with more of the observed variance attributed to scales > 2 m for the July sampling. This change may be attributed to the removal of sheep and the associated local inputs of N, combined with N fertilisation of the field (60 kg N ha^{-1}) that occurred 3 weeks prior to the second nested sampling event.

4.2. Optimisation of planning a within-field soil N sensor network

This study clearly demonstrates how nested sampling combined with geostatistical analysis can be used to explore how varying sensor-logger numbers and configurations affect the degree of accuracy of a field mean estimation. Furthermore, given knowledge of logger and sensor costs it is possible to rationalise planning decisions on a cost-accuracy basis. Given the unit costs of £2000 and £200 respectively for a data logger and NO_3^- ISE, the field mean for NO_3-N concentration could be estimated with a 95% confidence interval no wider than ± 1 µg N g^{-1} for a cost of £8,200. This would represent a significant cost to the farmer and may prevent anything significant uptake of the technology. The data logger and NO_3^- ISEs used for the cost calculation were chosen as they were used previously in this thesis (*Articles III* & *IV*). There is currently a wide range of similar devices, with a range of costs, currently on the market so the figures for the cost of implementing a sensor network described above should not be considered absolute. Furthermore, it is likely that the cost of the technology will continue to fall.

542 It is important to note that the data used for these calculations was derived from the
543 nested sampling which used a soil corer of 1 cm diameter. As such, these calculations are
544 based on the assumption that any given sensor used for the within-field network would have a
545 similar sized sampling volume. Results derived from the aggregate-scale sampling exhibited
546 variation at the sub 1-cm scale, which for NH_4-N and NO_3-N was an order of magnitude
547 larger than the 1-cm scale. This will have significant implications when using sensors with
548 sensing areas of size < 1 cm. More local replication at the sub 1-cm scale and hence an
549 increase in the size of sensor arrays would be required for an acceptable level of accuracy to
550 be achieved, resulting in increased costs. To explore optimisation of a network of sensors
551 with sensing areas < 1 cm, further sampling using sample volumes of < 1 cm would be
552 required. Ideally this would involve a similar level of replication, across all scales, to that
553 which was used in the July nested sampling campaign. This evidence may also be quite
554 instructive for optimising sensor design, as sensors with larger sampling areas will
555 encompass more of this small-scale variation.

556 Within this optimisation, no consideration has been made to the observed depth
557 effects. The resulting field mean is therefore, only applicable to the 5-10 cm depth. Rooting
558 depth, and therefore, nutrient uptake, in fields adjacent to the study site has previously been
559 observed to a depth of 30 cm (Jones et al., 2004). As such, any quantification of plant-
560 available N derived from the sensor network should be adjusted for observed depth effects. In
561 the case of cereals, which may root to depths >1.5 m, both topsoil and subsoil sensors will
562 probably be required to avoid bias and gain a representative pattern of soluble N within the
563 field. Logistically, however, the deployment of sensors in subsoils represents a significant
564 challenge.

565

566 *4.3. Potential for precision agriculture*

567 Integration of this approach it to a PA framework requires some further consideration.
568 PA, with regard to N management, has often focused on within-field spatial variation and the
569 identification of management zones to enable variable rate fertilisation, which is often
570 referred to as site-specific N management (SSNM) (Ferguson et al., 2002; Franzen et al.,
571 2002; Bongiovanni and Lowenberg-DeBoer, 2004; Cui et al., 2008). As the field used in this
572 study was broadly homogenous in its soil type and topography, which was reflected in the
573 observed small variation of soil N at large scales, it was considered more suitable to treat the
574 field as a single management unit with a singular mean value rather than impose MZs.
575 However, the importance of temporal variation for N management should not be
576 underestimated. Temporal variations in growing conditions, both within and between seasons
577 may lead to considerable differences in optimum N fertiliser requirement and hence,
578 inefficiencies in N fertiliser-use if temporal variations are not considered (Lark et al., 2003;
579 McBratney et al., 2005; Shahandeh et al., 2005; Shanahan et al., 2008; Deen et al., 2014).
580 It is important to consider how the approach used in this study could be applied to
581 field exhibiting significant random and non-random (i.e. a gradient) large-scale variation,
582 which might benefit from SSNM. It is possible that management zones could be delimitated
583 based on *a priori* knowledge of variables that may affect or indicate soil N status such as
584 topography (Kravchenko and Bullock, 2000), soil type (Moral et al., 2011), yield variability
585 (Diker et al., 2004) and farmers knowledge (Fleming et al., 2000). Alternatively, proximal or
586 remote sensing, such as electromagnetic induction, may allow rapid and cost effective
587 identification of large scale heterogeneity of soil physical properties (Hedley et al., 2004;
588 King et al., 2005). However, the extent to which these variables correlate to soil N
589 concentration is likely to be site specific and so may require some ground truthing. The need
590 for management zones should become apparent from exploratory sampling but accurate
591 delimitation of areas with significantly different soil N concentration may require sampling at

a finer resolution by increasing the extent of the stratification accordingly. A further broad question which needs to be addressed with respect to management zones, is at what point does the magnitude and the spatial-scale of soil N variation become sufficiently large enough to justify site-specific agriculture?

The success of the approach used here to optimise a sensor network and that of any management zone based system requires temporal stability of spatial variation (Sylvester-Bradley et al., 1999; Shi et al., 2002). Given significant spatio-temporal interaction, the results from any sensor network could no longer be considered accurate or precise. In this study there was evidence of a slight spatio-temporal interaction which was related to the removal of sheep from the field and the application of N fertiliser. An alternative approach to that advocated here, would be the implementation of a grid network, with sensor arrays at each node to account for small-scale soil variation. This would enable temporal, large-scale spatial variation and their interaction to be monitored. Kriging techniques could then be used to produce dynamic maps of soil N concentrations which could be used to inform variable-rate fertiliser management. However, this approach is likely to require significantly more sensing units and hubs with a resulting cost increase.

5. Conclusions

In this study, the spatial variation of amino acids, NH_4^+ and NO_3^- within the soil of a grazed grassland field was investigated using a nested sampling approach and geo-statistical analysis. Variation at small scales (< 2 m) was shown to be dominant, with further large variance evident at scales < 1 cm. The observed variation was attributed to the random input of N to the soil via sheep excreta and the inherent heterogeneity of soil at the aggregate scale. Optimising the deployment of in-situ soil sensors, on the basis of accuracy and cost, was demonstrated using data derived from the nested sampling and showed that achieving

617 accurate estimates of the field mean comes at a considerable cost. Whilst the cost of
618 technology is likely to decrease, investigation of how best to integrate this approach within a
619 PA framework to improve NUE is still required.
620
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625
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Figure legends

Fig. 1. The optimised sampling design of a mainstation. Distances between sampling points were fixed but angles were randomized, with the exception of the 2 m vectors.

Fig. 2. Accumulated variance components from the finest to coarsest spatial scale, derived from 5th and 6th June nested sampling results (before fertiliser addition). Source is the spatial-component in meters, with M and S representing the between-mainstation and between-strata components respectively.

Fig.3. Accumulated variance components from the finest to coarsest scale, derived from 31st July and 1st August nested sampling results (after fertiliser addition). Source is the spatial-component in meters, with M and S representing the between-mainstation and between-strata components respectively.

Fig. 4. Variability of amino acid-N, ammonium-N and nitrate-N with soil depth. Data points represent means ± SEM (n = 12) of soil N concentrations for each 5 cm depth increment.

Fig. 5. Width of the 95% confidence interval for alternative sensor arrays of different cost computed from variance components from nested sampling of nitrate N in (a) June (before fertiliser addition) and (b) July-August (after fertiliser addition). Note that the arrays comprise 1–10 loggers and a maximum of 15 sensors per logger. To allow a common range of values on the ordinates of these graphs, and to facilitate interpretation, arrays with fewer than five sensors in total have been excluded from Figure 5(a) and arrays with fewer than three sensors have been excluded from Figure 5(b).